REACTIONS OF 2, 8-DIHYDROXY-1-NAPHTHALDEHYDE

BY

DONALD EUGENE BURNEY

B.A., University of South Dakota, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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ACKNOWLEDGMENT

The author expresses his sincere appreciation to Professor Roger Adams, who suggested and directed this investigation.

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INTRODUCTION

The structure of gossypol, the yellow pigment in the cotton seed, has been established by Adams and coworkers [1] as 2,2-bi-1,6,7-trihydroxy-3-methyl-5-isopropyl-8-aldehydo-naphthyl. Three tautomeric forms have been postulated to account for the products formed when gossypol or gossypol hexamethyl ether reacts with certain reagents.

When heated at its melting point or when boiled with toluene, gossypol loses two molecules of water intramolecularly, giving an anhydro derivative.[2] Gossypol hexamethyl ether does not react with phenylhydrazine or hydroxyl amine in a neutral solution, but in glacial acetic acid the derivatives are formed, accompanied by the loss of two methoxyl groups.[3] The oxime then dehydrates to a *peri*-naphthoxazine derivative.

This investigation was undertaken to discover whether 2,8-dihydroxynaphthaldehyde would react in similar tautomeric forms since no such rearrangements have previously been described in the naphthalene series.

EXPERIMENTAL AND DISCUSSION

2,8-Dihydroxynaphthaldehyde [4] was prepared from 1,7-dihydroxynaphthalene using the Gattermann reaction with the modification of Adams and Levine.[5] This aldehyde could not be dehydrated to yield an anhydro derivative.

The 2,8-dimethoxynaphthaldehyde, prepared by methylation, reacted normally with phenylhydrazine and hydroxyl amine. The oxime dehydrated readily to 2,8-dimethoxynaphthonitrile.

2,8-Dihydroxynaphthaldoxime, isolated in only one form, with cold acetic anhydride dehydrated to 4-hydroxy-1,2-*peri*-naphthoxazine. Warm acetic anhydride acetylated the latter to 4-acetoxy-1,2-*peri*-naphthoxazine, and refluxing acetic anhydride and sodium acetate produced 2-acetoxy-N-acetyl-*peri*-naphthoimidolactone. The structure of the last compound was deduced from its hydrolysis with hydrochloric acid to 2-hydroxy-*peri*-naphtholactone, which could be methylated with diazomethane or acetylated with acetic anhydride. The 2-methoxy-*peri*-naphtholactone hydrolyzed with hot alkali and the product methylated to methyl 2,8-dimethoxy-naphthoate.

Methylation of the orthoxazine gave 4-methoxy-1,2-*peri*-naphthoxazine which reacted with acetic anhydride and sodium acetate

forming 2-methoxy-8-acetoxynaphthonitrile. This compound hydrolyzed to 2-methoxy-8-hydroxynaphthonitrile with hydrochloric acid, showing that it was not an imino ether as in the acetoxy series above. The 4-methoxy-1,2-*peri*-naphthoxazine was converted directly to the above product with alkali. This compound was methylated to 2,8-dimethoxynaphthonitrile, which was the same as the one obtained previously.

The methoxy- and acetoxy-naphthoxazine did not react the same with the same reagents. This may be a result of a stereochemical factor which allows the imino ether to form in one case and not in the other.

These reactions of 2,8-dihyhroxynaphthaldehyde can best be explained on the basis of the usual aldehyde structure, and no reactions of tautomeric forms were observed. The conclusion drawn is that in order to obtain tautomeric forms additional groups probably must be present. An hydroxyl group in the 3-position, it is predicted, will cause the tautomers to form.

SUMMARY

The reactions of 2,8-dihydroxynaphthaldehyde and its dimethoxy ether do not parallel those of gossypol, but rather yield the products expected from a normal aldehyde structure. Other substituents, primarily a 3-hydroxyl group and perhaps others, apparently have to be present to give the desired tautomerization.

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VITA

The author was born near Hartington, Nebraska, on October 17, 1915. He attended a rural school near Hartington and was graduated from Hartington High School in 1933. He received the degree of Bachelor of Arts from the University of South Dakota in 1937. In the fall of the same year he entered the Graduate School of the University of Illinois as a teaching assistant in inorganic chemistry. He held the appointment of teaching assistant for the years 1937-1941.

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